W00-3292-10

CONF-731086--1

SEDIMENT-WATER EXCHANGE IN CHESAPEAKE BAY

Owen P. Bricker III¹

and

Bruce N. Troup¹

Dept. of Earth and Planetary Sciences ✓

The Johns Hopkins University

Baltimore, Maryland 21218

Will be published in Proceedings of the Second International
Estuarine Conference.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Abstract

In Chesapeake Bay, diagenetic reactions in the sediment-interstitial water environment result in the enrichment of many dissolved species relative to their concentrations in the overlying water. Rapid exchange of dissolved species across the sediment-water interface in response to physical and chemical processes leads to the establishment of strong gradients in these species in the upper meter of the sediment column. In spite of the non-equilibrium nature of the overall system, the concentrations of species that participate in reactions whose time scales are rapid relative to their transport through the system, can be adequately described in terms of equilibrium models. The concentrations of chemically non-reactive dissolved materials and species that are involved in slow reactions relative to movement through the system, must be modeled on the basis of non-equilibrium diffusional transport.

Sediment-Water Exchange in Chesapeake Bay

Introduction

Estuaries are complex systems which receive chemical inputs from a variety of different sources (Fig. 1). River runoff contributes dissolved species derived from chemical weathering of rocks in the watershed, suspended material from mechanical weathering of terrigenous matter, and dissolved and particulate organic material of biogenic origin. The influx of sea water provides a strong electrolyte solution of nearly constant relative composition with respect to the major ions Ca^{++} , Mg^{++} , Na^+ , K^+ , Cl^- , and $\text{SO}_4^{=}$, as well as dissolved and particulate organic material and suspended sediment. Superimposed on the natural sources are inputs resulting from the activities of man.

The estuary is an open system in which the inputs are balanced by outputs in the form of flow through the system and sinks within the system. Some of the more soluble elements pass through the estuary to the ocean essentially unchanged, whereas others may combine and precipitate as solid phases or settle to the bottom sorbed on particulate matter to be stored in the sediment reservoir. Some materials also leave via atmospheric pathways. The biogeochemical characteristics of each element determine the type of behavior exhibited in its passage through the estuarine system. The balance between the inputs and the outputs of the elements, together with the physical flow regimen, determines the overall chemistry of the estuary.

The least understood component of the system is the influence of the sediment reservoir on the chemistry of estuarine waters. The sediment and its contained pore waters may be either a source or a sink for dissolved species depending upon the reactions that take place between pore fluids

and sediment and the direction of transfer of material across the sediment-water interface.

We have been investigating the chemistry and mineralogy of the interstitial water-sediment system of the Chesapeake Bay in an attempt to define the reactions that occur in this system, to evaluate their diagenetic significance, and to assess the effect of these reactions on the overlying waters of the bay in response to transfer of material across the sediment-water interface.

The Chesapeake Bay Estuary

The Chesapeake Bay is one of the earth's major estuarine systems. It dominates the mid-Atlantic seaboard and is the receiving basin for rivers draining much of the land area comprising southern New York state, Pennsylvania, Maryland and Virginia (fig. 2). The Susquehanna River supplies nearly 90% of the fresh water input to the bay above the mouth of the Potomac River, and approximately 50% of the total fresh water input to the entire bay. The Potomac and James Rivers supply the major portion of the additional fresh water input. (Table 1). Annual mean discharge into the bay from the entire watershed is approximately 2200 meters³/sec (Wilson and others, 1967; USGS Estimated stream discharge entering Chesapeake Bay, 1950-1973). The water discharged by the rivers carries dissolved and particulate materials to the bay. Particulate matter is also derived from shoreline erosion (Singewald and Slaughter, 1949; Schubel, 1968).

In addition to the river-borne dissolved constituents, tidal mixing transports sea salts into the estuarine system. The seasonal salinity distribution in the bay, resulting from mixing of river water with sea water, has been well documented by the Chesapeake Bay Institute (Seitz,

1970). Salinity varies from less than 1 ‰ in the vicinity of the mouth of the Susquehanna, to nearly normal sea water salinity at the mouth of the bay. In early spring when river discharge is high, salinities in the bay are lowest. As river discharge decreases throughout the summer and fall, salinities increase up the bay in response to the decreasing ratio of river water to sea water. On an annual basis, the estuarine system is filled approximately half by sea water and half by river water.

Solids carried to the bay by rivers consist of highly weathered materials from the watersheds. The coarser sediments collect near the mouths of the rivers, and the bay proper receives predominantly fine silt and clay size particles. A major portion of the silt size fraction is quartz. Quartz also persists through the clay size range, but declines in abundance with decreasing size fraction. The finer fractions consist primarily of illite and chlorite, with traces of kaolinite and montmorillonite. Small amounts of presumably authigenic phosphates, carbonates and sulfides are also present. Additionally, rivers transport to the bay large amounts of iron in the form of hydrous oxide coatings on mineral grains.

Schubel has estimated that the mean sedimentation rate in the bay is on the order of 2-3 mm/year. Estimates of sedimentation rates in this type of environment may be misleading, however, as flood discharge from tropical storm Agnes deposited an amount of sediment in the bay in a one-week period equivalent to perhaps 100 years of normal sedimentation. High intensity, infrequent storms of the Agnes type are probably much more important agents in terms of deposition of sediment in the bay, than are the normal daily transport and accumulation mechanisms. The bottom of Chesapeake Bay is blanketed by up to 60 meters of recent sediment. Data concerning the distribution of sediment types and the geometry of the sediment cover, however, are limited (Ryan, 1953; Biggs, 1967; Schubel, 1968).

Sediment-Water Exchange

The nature of the sediment-interstitial water environment is determined by a number of factors. As sediment accumulates, bay water is entrained and trapped in the interstices between sediment particles. Initially, then, the interstitial water has the same composition as the bottom water at that locality in the bay. As sedimentation continues, water and sediment which were at the top of the sediment column become increasingly deeply buried beneath the sediment-water interface. There is no longer free exchange with the overlying water, and chemical and biological processes begin to exert an influence on the composition of both the sediment and its contained water. If the organic content is large, as is usually the case with estuarine sediments, bacterial activity establishes strongly reducing conditions within a short distance below the sediment-water interface. Hydrous iron and manganese oxide coatings on mineral grains carried to the bay by rivers become unstable and dissolve. Sulfate is reduced to sulfide during bacterial oxidation of organic material with a concomitant production of bicarbonate and release of phosphate. Dissolved iron may react with sulfide, phosphate or carbonate to form new minerals in the sediment-pore water system. Clays undergo a shift in the relative proportions of cations occupying exchange sites (Russell, 1970) and may undergo exchange of iron for magnesium in their structures (Drever, 1971).

As a result of reactions of these types, the chemical environment of the pore water is very different from that of the overlying water even at shallow depths beneath the sediment-water interface. If the sediment-pore water system were completely isolated from exchange with the water column upon burial, the bulk composition of the system would remain

constant and changes would be limited to recombinations of the species present in the solids and aqueous phase. However, in the high porosity sediments of the upper meter, diffusion of dissolved materials readily occurs both within the sediment column and across the sediment-water interface. In addition to diffusional transport, the activities of burrowing benthic organisms, movement of sediment by storm generated waves and currents, and disturbance of the sediment by internally generated gas bubbles resulting from the decay of organic matter, may all contribute locally to the transfer of material across the sediment-water interface. The net result of these processes is the establishment of gradients in the concentrations of dissolved species in the pore water of the sediment column. Information necessary for understanding the chemistry of the estuarine system thus includes a knowledge of (1) the reactions occurring in the sediment reservoir that take up material from, or release material to the interstitial waters, and (2) the mechanisms and rates of transfer of material across the sediment-water interface. Equilibrium models are useful in identifying the reactions occurring in the sediment reservoir, and diffusion models are useful in determining the rates of transfer of materials within the sediment and across the sediment-water interface.

The Sediment-Interstitial Water System

In order to understand the reactions occurring in the system, it is necessary to have a knowledge of the chemical composition of the aqueous phase and the nature of the solid phases present. Our sampling program has been primarily oriented toward obtaining data on the interstitial water compositions of the upper meter of Chesapeake Bay sediments along

the salinity gradient of the bay. At each sampling locality the gross mineralogy of the sediments was also determined, and detailed examinations for certain minor phases were made.

Samples were taken along the axis of the Bay from Turkey Point to Wolf Trap Lighthouse and, in addition, station 856 was sampled monthly for a period of a year (Fig. 3). In all of the sampling operations a modification of the Benthos gravity coring apparatus was used.

Ten samples from each core were examined. The upper ten centimeters of cores were sampled in successive 2 cm layers and the rest of the core was sampled in 5 to 8 cm layers at depths of 15, 20, 40, 70, and 100 cm. These sample intervals were chosen on the basis of observed gradients in dissolved species with depth in our initial cores.

The water content of the upper meter of sediments ranges from nearly 85% (wt%) at the sediment-water interface to approximately 60% at a depth of one meter. Although the water content of these sediments is very high, they are sufficiently cohesive to allow dissection and sampling without destroying sedimentary structures.

The samples whose interstitial water was to be analyzed were extruded directly from the core into nylon squeezers of the type described by Reeburgh (1967). The pressure of nitrogen gas acting against a rubber diaphragm compressed the sediment and expressed interstitial water through a 0.22 μ m membrane filter. In this operation a portion of the water sample was diverted directly from the squeezer into an electrode cell for measurement of pH, $pS^=$, platinum electrode potential, and temperature. Another portion of the sample was collected in tubes containing acidified o-phenanthroline for iron analysis. The remainder of the sample was collected in a poly-

ethylene bottle from which aliquots were removed for shipboard analysis of other dissolved constituents. The samples were then acidified and refrigerated for onshore analysis of the major cations. Our analytical techniques are summarized in Table 2.

At the start of our interstitial water sampling program, we noted that reproducible results for iron and phosphate could not be obtained. We initially attributed this effect to temperature and/or pressure changes existing between the bay bottom and the shipboard laboratory. The squeezing of duplicate sediment samples at different temperatures and pressures failed to produce any differences in the behavior of iron and phosphate. Further investigation of this phenomenon disclosed that ferrous iron was oxidized during the short period of exposure of the sediment samples to the atmosphere during the extruding and squeezing operations. The resulting ferric compound removed phosphate and trace metals, which lead to erroneously low values for these species and iron.

We subsequently developed a procedure for handling the core and carrying out all sample manipulations under an inert atmosphere (Bray, et al, 1973). This procedure permits sampling and analysis of reducing waters, rich in ferrous iron, without losses of dissolved species due to oxidation effects (Fig. 4).

Interpretation of the reactions between the aqueous phase and solids requires knowledge of the activities of the aqueous species. In order to evaluate the activity of a dissolved species it is necessary to know, in addition to its concentration, the ionic strength of the solution in which it occurs. In the Chesapeake Bay the major ionic species in the overlying waters and in the sediment pore waters are Na^+ , Mg^{++} , Ca^{++} , K^+ , and Cl^- . The ionic strength of the waters is largely determined by these ions,

with some additional contribution from $\text{SO}_4^{=}$ and HCO_3^- . The waters, therefore, were analyzed for these species to provide the necessary information to permit realistic calculations of chemical equilibria in the system.

We have used the iron-phosphate-bicarbonate system as an example to illustrate the application of equilibrium modeling to the Chesapeake Bay system. The analytical data for iron, phosphate, and carbonate alkalinity in cores taken at stations along the axis of the bay are shown in figures 5 and 6. The most striking features of these data are the steep gradients observed in the upper part of the sediment column. The gradients imply fluxes of material both within the sediment column and across the sediment-water interface, pointing up the potential significance of the bottom sediments as a source for chemical species in the estuary. The observed changes in concentration suggest that the interstitial water reservoir behaves as an open system. Even though the steep gradients imply fluxes of material across the sediment-water interface, species that undergo chemical reactions whose rates are rapid with respect to the time scale of transport of these species through the system may approach equilibrium in the system. The concentrations of species that behave in this manner will be controlled at each point in the system by the reaction and can be modeled in terms of the appropriate equilibrium expression.

Equilibrium Modeling

Chemical equilibrium can only be closely approached if the residence times of the reacting species are long enough to allow completion of kinetically limiting reactions. For homogeneous aqueous solutions the kinetics of the reactions are so fast that equilibrium is usually closely

approached. A good example is the equilibrium model developed by Garrels and Thomson (1962) which accurately predicts the distribution of dissolved species in sea water.

The kinetics of reactions between solid phases and solutions are slower than those of homogeneous reactions; therefore, longer residence times are required to approach equilibrium. It has usually been found that overlying waters are rarely in equilibrium with the sediments below them because of the short residence time of the overlying water in contact with the sediment. In contrast interstitial waters are ideal natural environments in which to investigate equilibrium between solids and aqueous phases because of the long residence times of the aqueous phase. Furthermore heterogeneous chemical reactions may approach equilibrium faster in interstitial water because of the large ratio of solid surface area to water volume in fine grained sediments.

Simplifying assumptions are necessary to apply equilibrium thermodynamics to natural water systems. A model (MODAC) developed to compute the activities of various dissolved species and ion activity products of possible authigenic phases in the interstitial water of the upper meter of sediments of the Chesapeake Bay illustrates the typical assumptions and calculations inherent to the technique.

In MODAC the sediments were assumed to be an isobaric (1 atm), isothermal (25°C) system containing pure, stoichiometric solid phases. The deepest sediment core was sampled in 30 m of water; the resultant 3 atm difference between the in situ pressure and the assumed pressure negligibly affects the chemical equilibria. The temperature gradient in the upper meter of sediments was small, and the temperature averaged 24°C.

Although many of the solid phases of the sediments are probably not pure, X-ray diffraction patterns of our sediment samples indicate that essentially pure, crystalline siderite and vivianite are present.

Although it is not possible to measure individual ion activity coefficients, they can be estimated through the use of the Debye-Huckel approximation. There are several forms of the Debye-Huckel equation involving different numbers of fitted coefficients from which activity coefficients can be calculated. The form of the Debye-Huckel equation used in MODAC is

$$\log \gamma_i = - \frac{Az_i^2 \sqrt{I}}{1 + aB\sqrt{I}} \quad (1)$$

where A and B are constants for a given solvent at a specified temperature, a is the "effective diameter" of hydrated ions (a fitted parameter determined by Kielland), z_i the charge of the ion, γ_i the activity coefficient, I the ionic strength equal to $\frac{1}{2} \sum c_i z_i^2$, where c_i is the concentration of the ion i. Equation (1) represents the activity coefficients "with very good accuracy" up to an ionic strength of about 0.1 (Robinson and Stokes, 1970). The calculated ionic strengths in the northern Bay range from 0.02 to 0.36. The use of the Debye-Huckel equation for ionic strengths up to 0.36 results in a maximum error of 5% in the activity coefficient for monovalent ions and 13% for divalent ions, errors which approximate the accuracy of activity coefficients in a diluted sea water medium of $I = 0.4$.

The computation of the ionic strength, which is required for the calculation of activity coefficients, is facilitated in Chesapeake Bay sediment pore waters because of the constant cation-to-chlorinity ratio in

almost all the samples. Except for the station located at the mouth of the Susquehanna River, the concentrations of the major cations reflected those of a diluted sea water medium and could be predicted from the chlorinities. Thus, except for the station at the mouth of river, the contribution of the major cations to the ionic strength was calculated from the chlorinity. A significant fraction of the total sulfate and bicarbonate concentrations consists of ion pairs which reduce the contribution of sulfate and bicarbonate species to the ionic strength. To compensate for this it was assumed that only one-half of the analytical concentration of sulfate and one-tenth of the bicarbonate concentration contributed to the ionic strengths. Although the calculation of ionic strength in this manner is not exact, the difference between the ionic strengths calculated in MODAC and rigorously calculated ionic strengths does not exceed 2% along the salinity gradient of the bay.

The calculation of the distribution of the ferrous iron, phosphate, and carbonate species involves the manipulation of three mass balance equations. For pH's <7.7 and I<.39, which were the maximum values observed in Chesapeake Bay interstitial waters, the carbonate alkalinity can be expressed solely in terms of the bicarbonate ion.

$$CA = (\text{HCO}_3^-)_T = (\text{HCO}_3^-)_f + (\text{CaHCO}_3^+) + (\text{MgHCO}_3^+) + (\text{NaHCO}_3^0) \quad (2)$$

The mass action equations for the ion pairs are

$$K_a = \frac{a_{\text{CaHCO}_3^+}}{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}} = \frac{\gamma_{\text{CaHCO}_3^+} (\text{CaHCO}_3^+)}{\gamma_{\text{Ca}^{2+}(\text{Ca}^{2+})} \gamma_{\text{HCO}_3^-(\text{HCO}_3^-)}_f} \quad (2a)$$

$$K_b = \frac{a_{\text{MgHCO}_3^+}}{a_{\text{Mg}^{2+}} a_{\text{HCO}_3^-}} = \frac{\gamma_{\text{MgHCO}_3^+} (\text{MgHCO}_3^+)}{\gamma_{\text{Mg}^{2+}(\text{Mg}^{2+})} \gamma_{\text{HCO}_3^-(\text{HCO}_3^-)}_f} \quad (2b)$$

$$K_c = \frac{a_{\text{NaHCO}_3^0}}{a_{\text{Na}^+} a_{\text{HCO}_3^-}} = \frac{\gamma_{\text{NaHCO}_3^0} (\text{NaHCO}_3^0)}{\gamma_{\text{Na}^+(\text{Na}^+)} \gamma_{\text{HCO}_3^-(\text{HCO}_3^-)}_f} \quad (2c)$$

Substitution of the mass action equations for the ion-pairs into equation (2), use of the assumption that the activity coefficients of singly charged 1:1 ion-pairs and the bicarbonate ion are equal and those of neutral ion pairs are unity (Garrels and Thomson, 1962), and subsequent rearrangement yields

$$(\text{HCO}_3^-)_f = \frac{CA}{1 + K_a \gamma_{\text{Ca}^{2+}(\text{Ca}^{2+})} + K_b \gamma_{\text{Mg}^{2+}(\text{Mg}^{2+})} + K_c \gamma_{\text{Na}^+(\text{Na}^+)} \gamma_{\text{HCO}_3^-(\text{Na}^+)}_f} \quad (3)$$

which can be solved directly from the carbonate alkalinity, the concentrations of the cations, and the published stability constants of the ion pairs (Sillen and Martell, 1964).

The mass balance equations for ferrous iron and phosphate are

$$\begin{aligned} \text{Fe(II)}_T = & (\text{Fe}^{2+})_f + (\text{FeHPO}_4^0) + (\text{FeH}_2\text{PO}_4^+) + (\text{FeCl}_2^0) \\ & + (\text{FeCl}^+) + (\text{FeOH}^+) + (\text{FeSO}_4^0) \end{aligned} \quad (4)$$

$$\begin{aligned} P_T = & (\text{HPO}_4^{2-})_f + (\text{FeHPO}_4^0) + (\text{CaHPO}_4^0) + (\text{MgHPO}_4^0) + (\text{NaHPO}_4^-) \\ & + (\text{H}_2\text{PO}_4^-)_f + (\text{FeH}_2\text{PO}_4^+) + (\text{MgH}_2\text{PO}_4^+) \end{aligned} \quad (5)$$

Equations (4) and (5) can be rearranged and solved similarly to equation (3).

Solution of equations (3), (4), and (5) yields the free concentrations of ferrous iron, phosphate and bicarbonate. The product of the free concentrations and the appropriate single-ion activity coefficients gives the activity of each of the species.

The equilibrium state between sediment and interstitial waters depends on the stability of various solid phases. Carbonate, phosphate, sulfide and hydroxyl ion are the ligands with which iron commonly precipitates in natural water systems. The activities of sulfide in the northern Chesapeake Bay interstitial waters were so exceedingly small that effectively there was no free sulfide present in the interstitial water. Therefore, ferrous sulfide is not an important regulator of the solubility of ferrous iron. At the observed concentrations of bicarbonate and phosphate, it can be shown thermodynamically that ferrous hydroxide is unstable with respect to both siderite and vivianite in the interstitial waters of the Bay. Thus, in the sediments of the northern bay, carbonate and phosphate are the only two ligands capable of significantly affecting the ferrous iron solubility.

The calculated activities of ferrous iron, phosphate, and carbonate were used to derive the ion activity products of various solid phases including vivianite and siderite:

$$\log \text{IAP}_{\text{viv}} = \log a_{\text{Fe}^{2+}}^3 a_{\text{PO}_4^{3-}}^2 \quad (6)$$

$$\log \text{IAP}_{\text{sid}} = \log a_{\text{Fe}^{2+}} a_{\text{CO}_3^{2-}} \quad (7)$$

For convenience in comparing the saturation states of solids containing more than one cation and one anion, a log saturation function can be used to weight the deviation of the IAP from the solubility product, K_{so} :

$$\log \text{saturation} = \frac{1}{n} \log \frac{a_{\text{Fe}}^n a_{\text{X}}^m}{K_{\text{so}} (\text{Fe}_n \text{X}_m)} \quad (8)$$

Figure 7 is a plot of the log saturation values of siderite and vivianite computed from the composition of the interstitial water samples. Each level of several representative cores along the length of the Bay is plotted. (Note: the upper six points are from the upper 14 cm of the cores, the lower four points are from the lower 86 cm of the cores.) Positive log saturation values indicate supersaturation and negative values indicate undersaturation. For both siderite and vivianite the interstitial waters of the southern stations are just saturated with respect to the two solid phases. For both minerals the northern stations are slightly supersaturated, indicating that these minerals should be found in the sediments.

To investigate the equilibrium between these two minerals which possibly control the iron concentration in the interstitial waters, the activity of carbonate was plotted against the activity of phosphate for station 856-8. The theoretical boundary describing the equilibrium between siderite and vivianite is given by

$$K = \frac{a_{\text{PO}_4^{3-}}^2}{a_{\text{CO}_3^{2-}}^3} \quad (10)$$

$$\log a_{\text{CO}_3^{2-}} = 2/3 \log a_{\text{PO}_4^{3-}} + 1/3 \log K \quad (11)$$

Equation 11 was constructed on Figure 8, and the activities of the interstitial water samples from each level of two representative cores at station 856 were plotted on the figure. The close correspondence of the data points to the theoretical equilibrium line suggests that these pore waters are in equilibrium with both siderite and vivianite.

Many investigators have shown various natural water systems to be supersaturated with respect to certain solid phases, the implication being that the solids do indeed precipitate and influence the chemistry of the aqueous phase. However, it is not reasonable to assume that the compositions of the waters are controlled by the predicted solids without verification of the existence of these solids in the sediments.

We have identified vivianite and siderite in the sediments of the northern Chesapeake Bay using X-ray diffraction techniques. Examination of sediments for easily oxidizable phases such as vivianite requires minimum contact of the sample with oxygen. The effect of oxygen on reduced sediment is illustrated in figure 9, which shows three X-ray diffraction traces of the same sample run consecutively over a period of 30 minutes. The trace on the left was run five minutes after the slide was prepared, the second trace, three minutes later, and the final trace, 20 minutes after the second. Within the span of time needed for the three runs, the vivianite peak at $12.8^\circ 2\theta$ disappeared into the background.

The successful prediction of the presence of vivianite and siderite clearly indicates the advantages of an equilibrium model. Although the sediment-interstitial water system is not strictly a closed system, the equilibrium model does appear to adequately describe the behavior of these phases in the system.

The fact that equilibrium may exist at all levels in a core between the solution and a solid phase does not require that the activities of the species in solution be fixed, but only that the mass action equation be satisfied at all levels. If concentration differences exist between levels, diffusion will occur.

Diffusion

The simplest model of diffusive transport involves only molecular diffusion, which is described by Fick's first and second laws of diffusion:

$$J = -D \frac{\partial c_i}{\partial z} \quad (10)$$

$$\frac{\partial c_i}{\partial t} = D \frac{\partial^2 c_i}{\partial z^2} \quad (11)$$

where c_i is the concentration of the species i , z is depth, D is the diffusion coefficient, J is the flux of i through a plane normal to z , and t is time. Since spatial variations (x, y) are generally negligible compared to vertical variations, the diffusion equations can be expressed accurately in terms of depth (z) only.

The total variation of the concentration of i with respect to time due to all physical processes is given by:

$$\frac{dc_i}{dt} = \left(\frac{\partial c_i}{\partial t} \right)_z + w \left(\frac{\partial c_i}{\partial z} \right)_t \quad (12)$$

where $\left(\frac{\partial c_i}{\partial t} \right)_z$ is the local time rate of change of the concentration of i , $\left(\frac{\partial c_i}{\partial z} \right)_t$ is the concentration gradient of i at time t , and w is the rate of change of depth of a layer with time. During the deposition of sediments any given layer is progressively buried deeper. Thus, w represents a net rate of deposition, which can be measured empirically (Berner, 1971). The last term in equation (12) becomes important for long-term processes in sediments.

When the species i is involved in a chemical reaction, the total variation of the concentration of i with time is the sum of the effect of the chemical reaction on the concentration of i as well as the effect of diffusion. This can be expressed mathematically

as

$$\frac{dc_i}{dt} = D \frac{\partial^2 c_i}{\partial z^2} + \sum_j r_{ij} \quad (13)$$

where $\sum_j r_{ij}$ is the sum of the rates of change of the concentration of i with respect to time due to the reactions j (Berner, 1971). Substitution of equation (13) into equation (12) and rearrangement yields the local time rate of change of the concentration of i

$$\left(\frac{\partial c_i}{\partial t} \right)_z = D \frac{\partial^2 c_i}{\partial z^2} + \sum_j r_{ij} - w \left(\frac{\partial c_i}{\partial t} \right)_t \quad (14)$$

The relative importance of diffusion across the sediment-water interface can be determined by studying an ion which does not participate in any chemical reactions in the sediments, in which case the $\sum_j r_{ij}$ term in equation (14) disappears. Such an ion is chloride which is not involved in mineral equilibria or ion exchange reactions in brackish water sediments.

Many investigators have successfully modeled chloride diffusion across the sediment-water interface in fresh water lakes or in the sea with constant overlying water chlorinity (reviewed by Lerman, 1971; Tzur, 1971; Duursma and Bosch, 1971) or with monotonically increasing chlorinity over long periods of time (Lerman and Weiler, 1970). Few have attempted to model an estuarine system in which seasonal variations in the overlying water chlorinity occur such as those we see in the Chesapeake Bay.

Scholl and Johnson (1967) developed a model for chloride diffusion across the sediment-water interface in an estuarine system closely analogous to a heat conduction model described in Carslaw and Jaeger (1959). The chlorinity boundary condition at the sediment-water interface

is a sinusoidal function oscillating seasonally about a mean chlorinity value. For the short time scale relevant to seasonal transport processes in estuaries the last term in equation (14) can be neglected. The chlorinity-coredepth distributions generated by the Scholl and Johnson model closely mimic typical chlorinity distributions observed in Chesapeake Bay sediments (figure 10).

As can be seen in this yearly cycle of the distribution of chlorinity with depth of a typical station (858-8), significant monthly variations extend to 10 cm, while variations for the entire year extend to about 30 cm. These observations agree well with the expected thickness of a layer responding to diffusive transport from the overlying water calculated from equation 15.

$$\text{thickness of "diffusive layer"} = \sqrt{D \cdot t} \quad (15)$$

Using a diffusion coefficient of $3 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for the chloride ion in unconsolidated sediments (Lerman and Weiler, 1970) and a time scale of a month, the thickness of the diffusive layer is 9 cm. For a time scale of a year, the thickness is 31 cm.

The rapid exchange of chloride across the sediment-water interface can also be illustrated by data taken immediately after Tropical Storm Agnes in 1972. After Agnes record amounts of fresh water were discharged into the Chesapeake Bay. Figure 11 shows the excellent correlation between the minimum and maximum chlorinities in the overlying water and the upper 10 cm of interstitial water, which occurred respectively, in July and August of 1972. The chlorinity changes are most pronounced in the upper level of the core (0-2 cm) and are dampened with depth.

The calculation of the flux of chemically reactive species, such as iron and phosphate, across the sediment-water interface involves the use of reaction terms in the diffusion equation (13). The distributions with depth of iron and phosphate are determined primarily by diffusion, the rate of organic decomposition and the rate of controlling mineral equilibrium reactions. As discussed above, an important controlling mineral equilibrium reaction for phosphate is the vivianite equilibrium. Thus for phosphate the $\sum_j r_{ij}$ term in equation (13) represents the sum of the rates of production of phosphate from organic decomposition and the rate of precipitation or dissolution of vivianite:

$$\frac{dc_P}{dt} = D \frac{\partial^2 c_P}{\partial z^2} + \sum_j r_{P,j} \quad (16)$$

where $\sum_j r_{P,j} = \left(\frac{dc_P}{dt} \right)_{\text{organic decomposition}} + \left(\frac{dc_P}{dt} \right)_{\text{vivianite}} \quad (17)$

If the dissolution and precipitation of vivianite is diffusion controlled rather than surface reaction controlled, the last term in equation (17) can be expressed as a function of the departure from equilibrium

$$\left(\frac{dc_P}{dt} \right)_{\text{vivianite}} = k(c_P^{\text{eq}} - c_P) \quad (18)$$

where c_P^{eq} is the phosphate concentration in equilibrium with vivianite, c_P is the actual concentration in the interstitial waters and K may be a rate constant or may be a function of particle size. Equation (18) describes a process in which the larger the departure from equilibrium, the faster equilibrium is approached.

An apparent flux of phosphate across the sediment-water interface in the Chesapeake Bay has been calculated by Bray et al (1973) to be 9×10^{-3} $\mu\text{g-atom}/\text{cm}^2/\text{wk}$; in a week, a flux of this magnitude would transport enough phosphate across the sediment-water interface to increase the total phosphate content of the water column by 5%. However, this calculation represents a maximum value since reactions occurring at the sediment-water interface were not considered. Mortimer (1971) has pointed out that the existence of an oxidized layer inhibits sediment-water exchange due to coprecipitation reactions. In iron-rich environments the adsorption of phosphate on hydrous ferric oxides in an oxidized layer may greatly reduce the flux of phosphate (Bray et al, 1973).

The large apparent fluxes of ferrous iron across the sediment-water interface implied by the pronounced concentration gradients found in the upper 10 cm of Chesapeake Bay sediments (figure 5) are, of course, gross overestimates. Almost all of the ferrous iron diffusing upwards is precipitated upon contact with oxygen. The temporal variation of ferrous iron at any point in the sediment column, therefore, is the sum of several different chemical reactions as well as diffusion:

$$\frac{dc_{\text{Fe}}}{dt} = D \frac{\partial^2 c_{\text{Fe}}}{\partial z^2} + \sum_j r_{\text{Fe},j} \quad (19)$$

$$\text{where } \sum_j r_{\text{Fe},j} = \left(\frac{dc_{\text{Fe}}}{dt} \right)_{\text{reduction}} + \left(\frac{dc_{\text{Fe}}}{dt} \right)_{\text{vivianite}} + \left(\frac{dc_{\text{Fe}}}{dt} \right)_{\text{iron sulfide}} + \left(\frac{dc_{\text{Fe}}}{dt} \right)_{\text{siderite}} + \left(\frac{dc_{\text{Fe}}}{dt} \right)_{\text{oxidation}} \quad (20)$$

The vivianite, siderite and iron sulfide equilibrium terms can be expressed analogously to equation (18), the reduction term represents the rate of dissolution of limonitic ferric oxide coatings from fine-grained

sediment particles as a result of oxygen consumption in the sediments, and the oxidation term is the rate expression found by Stumm and Lee (1961):

$$\left(\frac{dc_{Fe}}{dt}\right)_{\text{oxidation}} = -k[C_{Fe}][O_2][OH^-]^2 \quad (21)$$

The insertion of exponential terms like those found in equations (18) and (21) renders the overall diffusion equation non-linear. As a consequence of the increased complexity introduced by these terms and the lack of data on the kinetics of many pore water-sediment reactions, rigorous solution of equation (20) is not possible at the present time. The equation does indicate, however, the type of data needed to model the exchange of chemically reactive species across the sediment-water interface and within the sediment column.

Acknowledgments

We thank John Bray, Virginia Grant, Rich Holdren, Mimi Uhlfelder, and the crew of the R/V Ridgely Warfield for their help in collecting and analyzing the samples. This work was supported by the Atomic Energy Commission, AEC AT(11-1)-3292.

Summary

We have attempted to illustrate the general behavior of the sediment-interstitial water environment and its importance to the chemistry of the estuarine system. In the Chesapeake Bay diagenetic reactions in the pore water-sediment environment result in the enrichment of many dissolved species by one or more orders of magnitude above that of their concentrations in the overlying water. Rapid exchange between overlying water and the upper part of the sediment column leads to the establishment of strong gradients in dissolved species extending to depths of at least 30 cm beneath the sediment-water interface.

Exchange of dissolved species across the sediment-water interface occurs in response to physical and chemical processes in the estuary. Scouring of sediments by tidal or storm induced currents and bioturbation of the bottom by benthic infauna lead to direct mixing and exchange of waters across the interface. Diffusion arising from concentration differences above and below the interface may result in transport of non-reactive species such as chloride through the sediment column and across the interface. Diffusion of chemically reactive species occurs in response to concentration differences coupled with chemical reactions which take place in the system.

Mechanical and biological transport mechanisms, because of their localized nature in time and space, are difficult to evaluate relative to their importance in the transfer of dissolved species across the sediment-water interface. Movement of non-reacting species in estuarine systems can be reasonably well approximated in terms of a simple diffusion model using an oscillating boundary condition to mimic seasonal variations in the

overlying water composition. In order to model the diffusion of chemically reactive species in the estuarine system, the controlling chemical reactions and their rates must be known.

Equilibrium models can be useful in identifying chemical reactions whose rates are rapid relative to the time scale of exchange and transport of participating dissolved species through the estuarine system. These models allow prediction of the concentrations of dissolved species involved in kinetically rapid reactions at any point in the estuarine system where such reactions occur. Chemically reactive dissolved species that participate in reactions whose time scales are slower than the time scale of movement of the dissolved species through the system are controlled by non-equilibrium transport processes. The concentration of these species must be described by more complex models involving diffusion and chemical reaction terms. Data of this type for systems as complex as the estuarine pore-water environment are not yet available; consequently the concentrations of species behaving in this manner cannot be accurately modeled at the present time.

References

- Berner, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill, N. Y. 240 p.
- Biggs, R. B. 1967. The sediments of Chesapeake Bay. In G. H. Lauff [ed.], Estuaries. Amer. Asso. Adv. Sci. Publ. 83, p. 239-260.
- Bray, J. T., O. P. Bricker, and B. N. Troup. 1973. Phosphate in interstitial waters of anoxic sediments: oxidation effects during sampling procedure. Science 180: 1362-1364.
- Carslaw, H. S. and J. C. Jaeger. 1959. Conduction of heat in solids. 2nd ed. Oxford University Press, Oxford, U.K., p. 51-67.
- Drever, J. I. 1971. Magnesium-iron replacement in clay minerals in anoxic sediments. Science 172: 1334-1336.
- Duursma, E. K. and C. J. Bosch. 1970. Theoretical, experimental and field studies concerning diffusion of radioisotopes in sediments and suspended particles of the sea. B. Methods and experiments. Netherl. J. Sea Research 4: 395-469.
- Garrels, R. M. and M. E. Thompson. 1962. A chemical model for sea water at 25°C and one atmosphere total pressure. Amer. J. Sci. 260: 57-66.
- Kielland, J. 1937. Individual activity coefficients of ions in aqueous solutions. J. Am. Chem. Soc. 59: 1675-1678.
- Lerman, A. 1971. Time to chemical steady-states in lakes and ocean. In J. D. Hem [ed.], Nonequilibrium Systems in Natural Water Chemistry. Advances in Chemistry Series 106, Am. Chem. Soc., Washington, D. C., p. 30-76.

- Lerman, A. and R. Weiler. 1970. Diffusion and accumulation of chloride and sodium in Lake Ontario sediment. *Earth Plan. Sci. Letts.* 10: 150-156.
- Mortimer, C. H. 1971. Chemical exchanges between sediments and water in the Great Lakes--speculations on probable regulatory mechanisms. *Limnol. Oceanogr.* 16: 387-404.
- Robinson, R. A. and R. H. Stokes. 1970. Electrolyte Solutions. Second edition (revised). Butterworth & Co., London. 571 p.
- Reeburgh, W. S. 1967. An improved interstitial water sampler. *Limnol. Oceanogr.* 12: 163-165.
- Russell, K. L. 1970. Geochemistry and halmyrolysis of clay minerals, Rio Ameca, Mexico. *Geochim. Cosmochim. Acta* 34: 893-907.
- Ryan, J. D. 1953. The sediments of the Chesapeake Bay. Dept. of Geol. Mines and Water Resources Bull. 12: 120 p. Md. Board of Natural Resources.
- Scholl, D. W. and W. L. Johnson. 1967. Effects of diffusion on interstitial water chemistry in deltaic areas. Seventh International Sedimentological Congress.
- Schubel, J. R. 1968. Suspended sediments of the northern Chesapeake Bay. Chesapeake Bay Inst. Tech. Rept. 35: 264 p. Reference 68-2. The Johns Hopkins University.
- Seitz, R. C. 1971. Temperature and salinity distributions in vertical sections along the longitudinal axis and across the entrance of the Chesapeake Bay (April 1968 to March 1969). Graphical Summary Rept. No. 5, Ref. 71-7, Chesapeake Bay Inst., The Johns Hopkins University, 99 p.

- Sillén, L. G. and A. E. Martell. 1964. Stability constants of metal ion complexes. Special publ. No. 17, The Chem. Soc. of London. 754 p.
- Singewald, J. T. and T. H. Slaughter. 1949. Shore erosion in tidewater Maryland. Md. Dept. of Geol., Mines, and Water Resources, Bull. 6, 140 p.
- Stumm, W. and G. F. Lee. 1961. Oxygenation of ferrous iron. Ind. Eng. Chem. 53: 143.
- Tzur, Y. 1971. Interstitial diffusion and advection of solute in accumulating sediments. J. Geophys. Res. 76: 4208-4211.
- USGS Estimated stream discharge entering Chesapeake Bay. Distributed by District Chief, USGS, Parkville, Md. 21234.
- Wilson, A. and others. 1967. River discharge to the sea from the shores of the conterminous United States. Hydrologic Investigations Atlas, HA-282. U. S. Geological Survey.

TABLE 1

River discharge to Chesapeake Bay*

<u>River</u>	<u>Discharge m³/s</u>
Susquehanna	1141
Potomac	388
James	284
All others	300

*Wilson and others, 1967; USGS Estimated Stream Discharge entering
Chesapeake Bay 1950-1972.

Analytical Techniques

Table 2

<u>Type</u>	<u>Species</u>
Colorimetric	Phosphate: molybdenum blue Ferrous iron: o-phenanthroline
Titrimetric	Carbonate alkalinity Chlorinity Sulfate
Potentiometric	pH Sulfide: Orion Ag^+/S^- electrode Eh: Pt electrode
Atomic absorption	Mg^{2+} , Ca^{2+}
Flame emission	Na^+ , K^+

Figure Captions

- Figure 1. Exchanges of matter in an idealized estuarine system.
- Figure 2. The drainage basin of the Chesapeake Bay.
- Figure 3. Sampling stations along the salinity gradient of the Chesapeake Bay.
- Figure 4. The effect of oxygen on the concentration of ferrous iron in squeezed interstitial water samples. Each data point represents a concentration of a 3 ml aliquot. A single sediment sample was homogenized and halved. One half (⊙) was squeezed exposed to the atmosphere. The second half (⊠) was squeezed in a glove bag filled with nitrogen gas. The maximum value was 4 ppm.
- Figure 5. Reactive phosphate and dissolved ferrous iron in the interstitial water of the upper meter of Chesapeake Bay sediments in August, 1972.
- Figure 6. Carbonate alkalinity in the interstitial water of the upper meter of Chesapeake Bay sediments in August, 1972.
- Figure 7. Log saturation plots of siderite and vivianite in the interstitial water at northern and southern stations in the Chesapeake Bay.
- Figure 8. Thermodynamic stability diagram for siderite, vivianite, and solution. The points represent the calculated activities of phosphate and carbonate from two cores at station 856-8. The straight line is the theoretical boundary separating the predominance areas of the two minerals.

Figure 9. Consecutive X-ray diffraction spectra of a single sample from station 914 for the angular span of $12.0-13.2^{\circ}2\theta$. The arrow indicates the major peak associated with vivianite.

Figure 10. The distribution with depth of chlorinity from 12 cores analyzed at monthly intervals at station 856-8.

Figure 11. The relation of the chlorinities in the sediment column to the chlorinities of the overlying water at station 856-8 for a one year period.

Fig 4

Fig 5

Fe CO_3 EQUILIBRIUM
IN INTERSTITIAL WATER

NORTHERN STATIONS

(—△—)

$\text{Fe}_3 (\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ EQUILIBRIUM
IN INTERSTITIAL WATER

SOUTHERN STATIONS

(—○—)

Fig 8

Fig 9